Characterization of Magnesium/Barium Aluminates Spinel Synthesized by Sol-Gel Auto-Combustion Method

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Nanocrystalline magnesium/barium aluminates powder was prepared by a sol-gel auto-combustion method from Al, Mg and Ba nitrates. Mg and Ba elements are among the potential candidates for various applications due to their flexibility, abundance and excellent electromagnetic performance. The phase transformation, crystal structure, functional groups, bonds in the structure and optical properties of the obtained powders were determined by X-ray diffraction, Fourier transform infrared spectroscopy (FTIR) and UV-visible spectroscopy. The electronic band gaps of MgAl2O4 and BaAl2O4 calculated using the Tauc method are shown to resemble largely unchanged as X (Mg or Ba) is substituted into the lattice, forming XAl2O4, but increase greater than 0.05 eV for MgAl2O4. The X-ray diffraction results reveal that with the X-substitution the crystallite size, cell volume and lattice parameter increase. The incorporation of magnesium and barium atoms into XAl2O4 is confirmed by the FTIR spectroscopy. The results show that MgAl2O4 and BaAl2O4 spinels can be obtained by sol-gel auto-combustion method at room temperatures (300 K), resulting in a material with high purity and large surface area.

Keywords: Magnesium alinate, Barium alinate, Spinell structure, Sol-gel method, Powder synthesis, Nanostructures.

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1. INTRODUCTION

Ceramic materials are known for their very interesting physical, chemical and mechanical properties, which differ according to the technique of synthesis and elaboration. The use and application of these materials are extensive such as in mechanical and electronic components, optical magnetic devices, tissue engineering magnetic storage systems and magnetic resonance imaging. Among these materials, aluminates (Al) based spinels with general formula XAl2O4 (where X = Mg and Ba) can be considered as a multifunctional material due to its numerous applications, in particular, in the military field: missile domes, transparent armor, thermal camera windows and rifleSCOPE. It is also used as catalysts in the environmental field, gas sensors and for energy storage and conversion [1-3]. Moreover, Al-based spinels are stable and environmentally friendly materials.

It has known that the synthesis method can affect the crystallinity, purity, particle size, surface area and morphology of nanoparticle XAl2O4, which exert a significant influence on their structural and optical properties [4]. XAl2O4 can be prepared by various techniques (sol-gel method, solid-state reactions and hydrothermal method), each of these techniques requires its own specialized equipment. The sol-gel auto combustion method has been demonstrated to produce homogeneous high-purity nanoparticles with rapid heating and short reaction time [5-7]. This synthesis method combines the chemical sol-gel and combustion process, representing a quick, accessible technique with low energy costs and ideal for the synthesis of materials based on metal oxides.

Here, we report the facile synthesis of MgAl2O4 and BaAl2O4 spinel-type oxides via simple approach of the sol-gel auto-combustion process. These samples are characterized by Ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis), Fourier Transform Infrared Spectroscopy (FTIR) and Powder X-ray diffraction (XRD) techniques in order to investigate their optical and structural properties. The present work aims to bridge the knowledge gap by utilizing the favorable properties of MgAl2O4 and BaAl2O4 samples to produce a potential candidate for various applications, such as catalysts, water treatment and refractory cements.

2. MATERIALS AND METHODS

2.1 Preparation of MgAl2O4 and BaAl2O4

MgAl2O4 and BaAl2O4 were synthesized by sol-gel auto-combustion method using a mixture of aluminum nitrate nonahydrate (sigma Aldrich, purity 99.99 %) and urea as complexing agent, with magnesium nitrate tetrahydrate (sigma Aldrich, purity 99.00 %), and barium nitrate (sigma Aldrich, purity 99.00 %) as precursors, respectively. All the chemicals were used as such without any further purification. The starting materials were supplied all in analytical pure grade (Merck-Germany). The different initial precursor quantities and chemical formula are shown in Table 1.

The stoichiometric proportions of aluminum nitrate, magnesium nitrate, barium nitrate and urea are dissolved in an amount of distilled water (100 ml). The mixture was heated to 200 °C while stirring constantly.

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After evaporation, the solution converts into wet gel. The gel is then heated at high temperatures in order to get a dry gel. Finally, the as-synthesized powders were calcined in air at 900 °C for 4 h. The sol-gel auto combustion method was used to prepare spinel type oxides (XAl₂O₄, X = Mg, Ba) in several steps, as shown in Fig. 1.

Table 1 – Quantity and chemical formula of the raw materials used to synthesize both structures

<table>
<thead>
<tr>
<th>Material</th>
<th>Chemical formula</th>
<th>Quantity (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum nitrate</td>
<td>Al(NO₃)₃·9H₂O</td>
<td>10.0</td>
</tr>
<tr>
<td>Magnesium nitrate</td>
<td>Mg(NO₃)₂·4H₂O</td>
<td>3.15</td>
</tr>
<tr>
<td>Barium nitrate</td>
<td>Ba(NO₃)₂</td>
<td>3.48</td>
</tr>
<tr>
<td>Urea</td>
<td>CO(NH₂)₂</td>
<td>5.35</td>
</tr>
</tbody>
</table>

2.2 Characterization Techniques

Crystallographic analysis of the nanoparticles obtained was performed using a PHILIPS PW 1800 powder diffractometer operated at 40 kV and 20 mA with radiation (λ = 1.54 Å) and scattering angle 2θ ranging from 10° to 90°. Spectroscopic analysis of the samples was carried out using FTIR in KBr pellets in the wavenumber range from 4000 to 400 cm⁻¹. Diffuse reflectance UV-Vis spectroscopy (SHIMADZU UV-1650-PC) in a wavelength range between 200 and 900 nm was used in order to find the optical properties and band gap energy (Eg) of the nanopowders obtained at room temperature.

3. RESULTS AND DISCUSSION

3.1 UV-Visible Analysis

In this part, the UV-Vis spectra of all samples were recorded in the wavelength range from 200 to 900 nm. Fig. 2 represents the UV-Vis transmittance spectra of MgAl₂O₄ and BaAl₂O₄ powders. Both structures exhibit better transmittance in the visible region of about 97% indicating good transparency of the studied samples. The absorption spectra of MgAl₂O₄ and BaAl₂O₄ samples are shown in Fig. 3. We observe that the two structures can efficiently absorb energy below 310 nm, allowing them to be considered UV activated photocatalysts. Additionally, it is possible to observe an absorption peak between 350 and 450 nm for MgAl₂O₄ and BaAl₂O₄.

Fig. 1 – The schematic flow chart for the formation of MgAl₂O₄ and BaAl₂O₄ nanocrystals by sol-gel auto-combustion method

Fig. 2 – UV-Vis transmittance spectra of MgAl₂O₄ and BaAl₂O₄ powders synthesized by sol-gel auto-combustion method

Fig. 3 – UV-Vis absorbance spectra of MgAl₂O₄ and BaAl₂O₄ powders synthesized by sol-gel auto-combustion method

In order to determine the optical energy band gap of both samples, the UV-Vis absorption spectrum was recorded (Fig. 3). This figure shows a strong absorption peak at 340 nm in the UV region. This can be attributed to photo excitation of electrons from the valence band to the conduction band. The value of the optical energy band gap (Eg) was estimated by the method proposed by Wood and Tauc, by extrapolating the linear portion of the Tauc’s graphs, according to the following equation [8, 9]:

$$E_g = \frac{hc}{\lambda_0}$$
\[
(\alpha \nu)^n = A(\nu - E_s),
\]

where \(\alpha\) is the absorption coefficient, \(\nu\) is the light energy, \(A\) is a constant, \(E_s\) is the band gap energy and \(n\) is a constant associated with different types of electronic transitions \((n = 1/2, 2, 3/2\) and \(3\) for direct allowed, indirect allowed, direct forbidden and indirect forbidden transitions, respectively).

The plots of quantity \((\alpha \nu)^2\) against \(\nu\) for \(\text{MgAl}_2\text{O}_4\) and \(\text{BaAl}_2\text{O}_4\) samples are represented in Fig. 4 and Fig. 5, respectively. From these curves, the point of intersection of the \(y\)-axis with the linear part gives an average value of the band gap equal to 3.676 eV for \(\text{MgAl}_2\text{O}_4\) and 3.626 eV for \(\text{BaAl}_2\text{O}_4\). From the above results, it can be noted that the change of \(X\) element caused the reduction in the band gap for magnesium (Mg) cation compared to barium (Ba) cation. A similar observation was noted by C. Gómez-Solís et al. [10].

Fig. 2 and Fig. 3 show the XRD patterns of \(\text{MgAl}_2\text{O}_4\) and \(\text{BaAl}_2\text{O}_4\) structures synthesized by sol-gel auto-combustion method, respectively. All observed peaks for both structures (\(\text{MgAl}_2\text{O}_4\) and \(\text{BaAl}_2\text{O}_4\)) match excellently with ICSD (Inorganic Crystal Structure Data base), data file No. 9010350 and 1010630, respectively. This result indicates the high-purity and crystallinity of these samples synthesized in this work.

![Fig. 6 – X-ray patterns of \(\text{MgAl}_2\text{O}_4\) nanoparticles synthesized by sol-gel auto-combustion method](image1)

![Fig. 7 – X-ray patterns of \(\text{BaAl}_2\text{O}_4\) nanoparticles synthesized by sol-gel auto-combustion method](image2)

From the XRD measurement data, we can calculate the crystallite size, lattice constant, and cell volume. The lattice parameters of the prepared samples were estimated from \(2\theta\) values of the most intense peak using the Bragg diffraction condition given by [11, 12]:

\[
a = \frac{\lambda}{2 \sin \theta} \left( h^2 + k^2 + l^2 \right)^{1/2},
\]

where \(\lambda\) is the wavelength of the X-ray radiation, \((hkl)\) signify the Miller indices, and \(\theta\) is the diffraction angle corresponding to the most intense reflection plane.

The unit volume \((V)\) of the prepared aluminate spinels was calculated using the expression [13, 14]:

\[
V = \frac{\sqrt{3}}{2} a^2 c.
\]

3.2 X-ray Diffraction Analysis

XRD was used to identify the crystal structure and phase evolution of powders prepared after calcination. According to this method, diffraction patterns are generated from a powdered sample of crystals and compared with reference cards within a database that contains diffraction patterns of known crystals.
The crystallite size is calculated from the full width at half maximum (FWHM (β) of the diffraction peaks using the Debye-Scherrer method [15, 16] according to the following equation:

\[ D = \frac{k \lambda}{\beta \cos \theta}, \]

where \( k \) is the crystallite shape factor (\( k = 0.89 \)), \( \lambda \) is the X-ray wavelength (\( \lambda = 1.5406 \) Å), \( \beta \) is the FWHM, \( \theta \) is the maximum of the Bragg diffraction peak (in radians), and \( D \) is the crystallite size estimated. The results obtained for the lattice parameter (a), crystallite size (D) and cell volume (V) for both samples are summarized in Table 2.

Table 2 – Values of the lattice constant, unit cell volume and average crystalline size calculated from XRD analysis for both samples (MgAl\(_2\)O\(_4\) and BaAl\(_2\)O\(_4\))

<table>
<thead>
<tr>
<th>Parameters calculated</th>
<th>MgAl(_2)O(_4)</th>
<th>BaAl(_2)O(_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>08.08</td>
<td>10.42</td>
</tr>
<tr>
<td>b (Å)</td>
<td>08.08</td>
<td>10.42</td>
</tr>
<tr>
<td>c (Å)</td>
<td>08.08</td>
<td>08.78</td>
</tr>
<tr>
<td>V (Å(^3))</td>
<td>527.53</td>
<td>825.58</td>
</tr>
<tr>
<td>D (nm)</td>
<td>20.07</td>
<td>34.66</td>
</tr>
</tbody>
</table>

3.3 Fourier Transform Infrared Data Analysis

FTIR analysis was performed to investigate the formation of the metal aluminate spinel structure and surface functional group. The study of atomic and molecular vibrations with the identification of local chemical bonds is possible with the aid of the peaks created in different regions of the IR spectra.

FTIR spectra of MgAl\(_2\)O\(_4\) and BaAl\(_2\)O\(_4\) were analyzed as represented in Fig. 8. Vibrations of the bonds in the region 400-600 cm\(^{-1}\) correspond to metal ions. The peaks present in this range are due to the presence of divalent metal cations (Mg–O and Ba–O) [17, 18]. MgAl\(_2\)O\(_4\) and BaAl\(_2\)O\(_4\) powders exhibit additional minor transmission bands at 2877, 2455 and 2363 cm\(^{-1}\). Transmittance bands shown by both powders at 3475 and 1746 cm\(^{-1}\) correspond to broad –OH stretching and H–O–H bending vibrations, respectively [19]. Additionally, the intense band at 1427 cm\(^{-1}\) confirms the asymmetric stretching of tetrahedral AlO\(_4\), indicating the formation of the MgAl\(_2\)O\(_4\) and BaAl\(_2\)O\(_4\) phase. This result is consistent with other works, in which powders were synthesized by solution combustion synthesis method similar to that studied in this work.

4. CONCLUSIONS

MgAl\(_2\)O\(_4\) and BaAl\(_2\)O\(_4\) nanopowders were prepared successfully using sol-gel auto-combustion method. This method results in materials with important properties for numerous applications. The variation of band gap values can be attributed to structural disorder in the structure, which may change the present energy levels within the band gap. Therefore, the value of \( E_g \) may depend on the type of cations present in the spinel structure and synthesis conditions. The XRD results prove the spinel phase for all samples with no secondary phase. The characteristic IR absorption bands in the frequency range of 400-800 cm\(^{-1}\) exhibited the expected main absorption bands, thereby confirming the spinel structure. The structural properties of spinel-type aluminates depend upon the method of preparation and the nature of the substituting element.

REFERENCES


Характеристика шпинелі алюмінатів магнію/барію, синтезованих золь-гель методом автогоріння

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Нанокристалічний порошок алюмінатів магнію/барію готували золь-гель методом автогоріння з нітратів Al, Mg та Ba. Елементи Mg і Ba є потенційними кандидатами для різних застосувань завдяки їх гнучкості, великої кількості у природі та чудовим електромагнітним характеристикам. Фазові перетворення, кристалічну структуру, функціональні групи, зв'язки в структурі та оптичні властивості отриманих порошків визначали за допомогою рентгенівської дифракції, інфрачервоної спектроскопії (FTIR) та УФ-видимої спектроскопії. Показано, що електронні ширини забороненої зони MgAl₂O₄ і BaAl₂O₄ зростають при заміщенні X-атомами Mg або Ba.

Результати показують, що порошок Х₂O₅ можна отримати золь-гель методом автогоріння при кімнатній температурі (300 К), що призводить до отримання матеріалу високої чистоти та великої площі поверхні.

Ключові слова: Алюмінат магнію, Алюмінат барію, Структура шпінелі, Золь-гель метод, Наноструктури.